STUDIES ON METAL COBALTITE (MCo_2O_4, M= Zn, Ni, Mg) AND GRAPHENE OXIDE BASED NANOCOMPOSITES FOR ENERGY STORAGE APPLICATION

A SYNOPSIS

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1. Introduction

Energy and its consumption are more important and unavoidable in the modern world. There are different forms of energy including chemical, electrical, thermal, light, mechanical, hydropower, ocean, wind, and nuclear energy. Global population growth and the economy's expansion have combined to impact the next generation and burden the electrical infrastructure seriously. The three main fossil fuels used in today's world are coal, oil, and gas and they are non-renewable. The energy crisis is exacerbated by a number of factors, including delays in power plant commissioning, underuse of renewable energy, insufficient distribution, serious accidents, natural disasters, overconsumption, poor infrastructure, energy waste, and an excess of people [1,2]. Although there are already alternative energy sources like wind turbines, solar cells, biomass plants, etc., these technologies have some drawbacks such as insufficient electrical energy storage. Due to the intermittent nature of this renewable energy, storage and supply are essential to maintaining a consistent supply of electricity to the devices. Modern electrical and electronic gadgets also require electrical supply and storage systems with a variety of energy and power capabilities to meet their requirements, which range from low to high. Therefore, it is necessary to develop a variety of unique energy delivery and storage solutions through the study of novel materials. To address these needs, a range of innovations in alternative energy storage devices, such as batteries, supercapacitors, and fuel cells, have been developed [3].

Supercapacitors (SCs) are widely used energy storage technologies that have extended cyclic lifetimes, high power densities, and high specific capacitance [4]. SCs, which have a higher power density than conventional capacitors, are also known as ultracapacitors and electrochemical capacitors. Since the capacitors can be swiftly charged and discharged, they are used for a range of electrical purposes [5]. SCs consist of two current collectors that are separated from one another, and two electrodes dipped in an electrolyte solution. The process of storing energy includes building up and releasing electrical charge on two conducting plates that are significantly apart from one another. SCs are utilized in a wide range of industries, including aerospace and military, portable electric vehicles, high-speed electric vehicles, flexible electronics, uninterruptible power sources for electronic devices, and flexible electronics. The need for energy storage is constantly growing as a result

of modern lifestyles, industrialization, and significant levels of carbon emissions. Due to the increasing importance of these technologies, scientists and engineers are keen to increase their effectiveness and lower their cost. Furthermore, a single material cannot be adequate for a wide range of applications. As a result, a variety of materials need to be investigated for various types of application needs.

Remarkable life span, excellent charge-discharge, very high power density with environmental friendliness are the awaited characteristics of supercapacitor (SCs) electrodes [6]. Based on their energy-storage method, the electrodes of SCs may be split into two categories: electric double layer capacitors (EDLC) and pseudocapacitors (PC). Metal-based oxides/hydroxides/sulfides, and conductive polymers etc., have the feature of pseudocapacitance and that allow fast faradic oxidation-reduction at electrode surface. It possess higher charge storage ability and power density [7]. EDLC can be exhibited by carbon materials with higher conductivity rate but with less charge storage ability. In most instances, the current capacity in both types is proportional to the electrode surface area that the electrolyte ions may access. The effectiveness of electrochemical energy devices is heavily reliant on electrolyte characteristics, electrode materials, rational device design, synthesis/functionalization processes, and so on. Hybridizing EDLC and PCs could be the wise choice to satisfy the energy needs of the future with better specific capacitance capabilities. Although, conventional metal oxides could not have been the better alternate and it should be enhanced optimally by chemical engineering. Reduced graphene oxide (rGO), one of the carbons EDLCs, has the potential to serve as a two-dimensional (2D) layer for distributing and adorning high PC nanoparticles. Due to physical interaction or chemical reaction at the surface or interface of the electrode and electrolyte, the structure of nanoparticles offers outstanding performance. In an experimental situation, pseudocapacitive materials can generate high capacitance values by chemical reactions, but they lack the necessary cyclic stability. Excellent cyclic stability and capacitance are features of electrical double layer capacitive (EDLC) materials. HCs are generated by combining both to address this issue and improve performance. Hybrid supercapacitors (HCs) have been developed to increase the device's power and energy density by combination of EDLC and PC electrode materials utilized. The construction of a hybrid supercapacitor might take many different forms [8].

The ability to engineer its electronic structure, light weight, superior conductivity, large surface area, flexibility, low cost, and high stability make the EDLC type of graphene oxide (GO) and reduced graphene oxide (rGO) attractive materials for hybrid supercapacitors fabrication. In addition, successfully altering the electrical environment and the inherent properties of these materials can be accomplished by chemically doping graphene oxide sheets with heteroatoms. The introduction of heteroatoms into the ideal hexagonal carbon sheet would unavoidably alter the characteristics of graphene, such as its thermal stability, charge transport, Fermi level, bandgap, localized electronic state, spin density, optical properties, and magnetic properties. Nitrogen, out of all the heteroatoms, is important for doping with graphene. The dopant nitrogen, which has a distinct electrical structure but an atomic size identical to carbon, stimulates N-type conductivity. Nitrogen incorporated within the graphene lattice considerably improves electrochemical performance. N atom plays a role as spacer and bridge to increase the interlayer distance between graphene sheets and electrically interconnecting the individual graphene sheets. Also, it allows to have a large surface area, quick electron conduction which facilitate rapid ion transfer in electrolyte [9]. As a result, the inner area of the electrode's active material may reach the electrolyte, increasing the specific capacitance. N-doping in the rGO skeleton, which permits two electrons to enter the rGO's π-conjugated networks. The defects arising from the doping process generate active sites and delocalization of positive charges over N-rGO, which increases the affinity with negatively charged ions via electrostatic interaction. Nitrogen doping alters the electrical structure of graphene by forming the pyrrolic, pyridine, and quaternary nitrogen bonds. The electric layers' density is increased as a result. The interfacial capacitance and material structure configuration are primarily responsible for the rise in the capacitive nature of N-doped graphene for supercapacitor electrodes [10].

Spinel structured oxides ($A^{2+}B_2^{3+}O_4^{2-}$) possess A^{2+} atoms at tetrahedral sites and B_2^{3+} at octahedral sites having a remarkable electrochemical, electrical, and magnetic properties [11,12]. The metal oxide Co_3O_4 in nanoscale have a high theoretical specific capacitance of 3560 Fg^{-1} due to rich oxidation states Co^{3+}/Co^{2} [13,14]. Zn, Ni, Mg based its oxides also have +2, +3 oxidation states and can be combined with Co_3O_4 produces $ZnCo_2O_4$, $NiCo_2O_4$ and $MgCo_2O_4$ spinels with high

theoretical specific capacitance. In the regular spinel structure, divalent M^{2+} (M= Zn, Ni, Mg) and trivalent Co^{3+} cations occupy tetrahedral and octahedral voids, respectively. In regular spinel, MO_4 (M= Zn, Ni, Mg) tetrahedra are unconnected, while CoO_6 octahedra share an edge. When tetrahedra cations move to octahedra sites, the inverse spinel is formed [15]. Transition metal oxides (TMO) are popular due to their low cost and environmental friendliness. TMOs have low electronic conductivity, which can be improved by using different preparation methods such as chemical, solid-state, and other methods. In order to design hybrid supercapacitors MCo_2O_4, (M= Zn, Ni, Mg) nanomaterials can be combined with the nitrogen doped graphene oxide (GO) and reduced graphene oxides (rGO). $ZnCo_2O_4$ has a substantially higher theoretical specific capacitance of 2604 Fg^{-1} [16]. $MgCo_2O_4$ possess higher theoretical capacitance of 3122 Fg^{-1} [16]. Ternary Nickel cobaltite $NiCo_2O_4$ has the theoretical specific capacitance of 2682 Fg^{-1} [16]. Though, high in theory cannot be experimental for all those metal cobaltite's. Therefore, research is called for that looks into the hybridization of graphene oxide with MCo_2O_4 metal cobaltite's in order to better suit the needs and applications of the next generation of energy storage.

Surprisingly, $ZnCo_2O_4$ is just the replacement of Co^{2+} with Zn^{2+} on Co_3O_4 and resulted in the spinel structure. Zn^{2+} occupies the tetrahedral sites and Co^{3+}occupies the octahedral sites [17]. Ternary nickel cobaltite $NiCo_2O_4$ has a spinal $A^{2+}B_2{}^{3+}O_4$ structure that can be formed by replacing one cobalt atom in Co_3O_4 with nickel. Redox pairs Co^{2+}/Co^{3+} and Ni^{2+}/Ni^{3+} can move during the charge-discharge process. The desired oxidation states confirm $NiCo_2O_4$'s significance for energy storage applications. Zn, Ni, Mg based oxides also have +2, +3 oxidation states and can be combined with Co_3O_4 produces $ZnCo_2O_4$, $NiCo_2O_4$, $MgCo_2O_4$, spinels with high theoretical specific capacitance. Due to high specific capacity and great cyclic rate capability cobalt-based metal oxides, such as $ZnCo_2O_4$, $NiCo_2O_4$ and $MgCo_2O_4$ are the excellent candidates for electrode applications [7,18]. Numerous past investigations focused on developing various nanostructured morphologies rather than investigating the heteroatom of nitrogen doped reduced graphene oxide-based nanocomposite. Graphene materials are combined with spinel metal oxide materials to create composites, which have both physical and chemical charge storage processes in a single electrode piece. This composite electrode has both the EDLC mechanism and

pseudocapacitance. The graphene-based composite electrode has a wide surface area, which enhances contact between the deposition of the pseudocapacitive material and the electrolyte solution and can increase the electrical double layer capacitance. Through the faradaic reaction, a pseudocapacitive material raises the capacitance of the composite electrode. Despite many syntheses route, chemical reflux is an effective way to prepare the nanocomposite with N-rGO and have more wettability between the electrodes and electrolyte [19,20]. So, the modification of the structure and graphene oxide is needed for enhancing the specific capacitances of it. The goal of this research is to functionalize graphene oxide by nitrogen incorporation and prepare the GO and N-rGO based $ZnCo_2O_4$, $NiCo_2O_4$ and $MgCo_2O_4$ nanocomposite for supercapacitor applications.

2. Literature Review

Xu et al. [21] reported that graphene oxide (GO) was produced using a modified Hummers method, resulting in the thinnest sheet structure of shape with a specific capacitance (Csp) of 189 Fg^{-1} for 1 Ag^{-1} and cyclic stability of 5000 cycles with only 7% decrease. According to research by Down et al. [22] the nanosheet structure of graphene oxide (GO) synthesized using the Hummers method exhibits a specific capacitance of 423 Fg^{-1}, energy density of 13.9 Wkg^{-1}, and power density of 11.6 $WhKg^{-1}$. Febre et al. [23] established that GO materials were synthesized using a modified Hummers method. The stacking of the sheets had the specific capacitance of 154 Fg^{-1} for 0.5 Ag^{-1} with 95% cyclic stability after 10,000 cycles. Boron doped GO has an EDLC Csp of 192.5 Fg^{-1}, according to research by Hyeok et al. [24]. Kill et al. [25] reported that low temperature reduced graphene oxide (rGO) had Csp of 240 Fg^{-1} approximately as well as energy and power densities of 33.3 $Whkg^{-1}$ and 833.3 Wkg^{-1}. Nam et al. [26] researched the rGO by chemical reduction. It was made up of many layers, and electrochemical testing shows that it possesses a Csp of 85.3 Fg^{-1} for 1 Ag^{-1}, which remained retention of 85% after 1000 cycles. Johra and Jung [27] synthesized rGO using hydrothermally to produce the graphene sheet layers with Csp 367 Fg^{-1} at 1 Ag^{-1}. Rajagopalan and Chung [28] followed the chemical reduction process for preparing rGO, which showed good cyclic stability up to 3000 cycles and a Csp of 253 Fg^{-1} at a current density of 0.2 Ag^{-1}. Hang et al. [29] demonstrated that substantially reduced graphene oxide was produced utilizing the solid phase approach and has a Csp of 128 Fg^{-1} for a current density of 1 Ag^{-1}. Looking at more reports,

we can find that the specific capacitances for the reduced graphene oxides made by various methods are more or less identical. Therefore, in order to develop and uncover novel functions for graphene materials and widen the range of potential applications, it is essential to have a complete understanding of how graphene characteristics may be altered by heteroatom doping and reduction processes. It is critical to develop straightforward, effective methods for producing nitrogen doped N-rGO and it is necessary to understand its behaviour with regard to the impacts of changing temperatures for the energy storage applications in both pristine form and in nanocomposites.

There are investigations being done for energy storage applications combining metal cobaltite and graphene oxides. Mary et al. [30] used the hydrothermal technique to investigate the rGO/$NiCo_2O_4$@$ZnCo_2O_4$ ternary nanocomposite material for supercapacitor applications. They reported that at a current density of 1 Ag^{-1}, 50 mg of rGO incorporation had a maximal specific capacity of 1197 Cg^{-1}. Wang et al. [31] team used ultrasonic processing, a one-step hydrothermal approach, to develop a $ZnCo_2O_4$/N-doped reduced graphene oxide/Ni foam substrate (ZNGN) electrode. The electrochemical test showed that the highest capacitance of the ZNGN electrode was 1600 Fg^{-1} at a current density of 1 Ag^{-1} in a 6 M KOH solution. Surface morphologies can be modified using several synthetic techniques to produce high specific capacitance. Patil et al. [7] designed it as Au@rGO-$ZnCo_2O_4$ nanomaterial, it exhibits a high specific capacity of 288.5 $mAh^{-1}g^{-1}$ at a scan rate of 2 mVs^{-1}. Mirzaeian et al. [32] reported that the Csp of the nitrogen doped resorcinol/formaldehyde carbon aerogels with regulated nitrogen concentration was 208 Fg^{-1} at 1 Ag^{-1}. Because the mineral basis of zinc and cobalt is plentiful in comparison to others, it can be a low-cost electrode for the application if greater specific capacitances are attained. The metal oxide N-rGO/$ZnCo_2O_4$ is a lesser-known nanocomposite and also less expensive if produced from the low temperature process. Numerous past investigations focused on developing various nanostructured morphologies rather than investigating the heteroatom of nitrogen doped reduced graphene oxide-based N-rGO/$ZnCo_2O_4$ nanocomposite.

Hassanpoor and Aghely [33] prepared hydrazine and ammonia functionalized N-rGO was used in a sonochemical process to produce a $NiCo_2O_4$/N-rGO nanocomposite with a maximum Csp of 618 Fg^{-1} at a current density of 4 Ag^{-1}.

Mondal et al. [34] reported rGO/$NiCo_2O_4$ composites hollow spheres reveals that 971 Fg^{-1} at a current density of 0.5 Ag^{-1}. Alhokbany et al. [35] made $NiCo_2O_4$@Nitrogen doped carbon with spherical morphology reveals that 913 Fg^{-1} at 1 Ag^{-1} with a retention of 99% after 4500 cycles. Jiang et al. [36] established that $NiCo_2O_4$/rGO nanowire which exhibits 931.7 Fg^{-1} at 1 Ag^{-1} and also delivered 83.8% retention over 5000 cycles. Shoo et al. [37] established that $NiCo_2O_4$ nanorods morphology synthesized by hydrothermal method and obtained Csp of 823 Fg^{-1} at 0.8 Ag^{-1} revealing that cyclic stability was 81% for 1000 cycles. Zhang et al. [38] established that $NiCo_2O_4$/Graphene synthesized by chemical vapor deposition method reveals the Csp 1402 Fg^{-1} at current density of 1 Ag^{-1} with 76.6% retention after 5000 cycles. So far, N-doped graphene oxide (N-rGO), particularly made from urea with $NiCo_2O_4$ nanocomposite, has not been focused.

The high rate of electrochemical performance of the $MgCo_2O_4$ nanowire arrays on graphene coated nickel foam $MgCo_2O_4$/G-NF electrode was demonstrated by Guan et al. [39] and the Csp of 500 Fg^{-1} at a high current density of 50 Ag^{-1}. Vijayakumar et al. [40] established that comparison of $MgCo_2O_4$, the rGO/$MgCo_2O_4$ nanocomposite and found nanocomposite had a greater Csp of 570 Fg^{-1} at a current density of 1 Ag^{-1} with retention of 96% after 5000 cycles. In another research by He et al. [41], $MgCo_2O_4$@Ni_3S_2 core-shell nanocomposite had a Csp of 1123.1 Fg^{-1} at 1 Ag^{-1} in 2 M KOH electrolyte. The low-cost production of these metal cobaltite's and their nanocomposites with nitrogen doped graphene oxides might be considered as having a research gap based on these reviews of the literature. To fill this gap, the concept of nitrogen-doped reduced graphene oxides and metal cobaltite nanocomposites has been put forward.

3. Objective

The objectives of the present research studies are,

- Synthesis of graphene oxide through modified hummers method and reducing as well as doping of nitrogen (N) with it by hydrothermal method.
- Preparation of MCo_2O_4, (M= Zn, Ni, Mg) nanomaterials such as $ZnCo_2O_4$, $NiCo_2O_4$, and $MgCo_2O_4$ using low-cost simple reflux method.

- Synthesis of graphene oxide (GO) loaded GO/$ZnCo_2O_4$, GO/$NiCo_2O_4$, GO/$MgCo_2O_4$ nanocomposites using low-cost simple reflux method.
- Synthesis of graphene oxide (GO) loaded N-rGO/$ZnCo_2O_4$, N-rGO/$NiCo_2O_4$ and N-rGO/$MgCo_2O_4$ nanocomposites using low-cost simple reflux method.
- Investigating thermal stability and phase changes of the synthesized MCo_2O_4, (M= Zn, Ni, Mg), GO, N-rGO and its N-rGO/MCo_2O_4, (M= Zn, Ni, Mg) nanocomposites by subjecting to TG-DTA analysis.
- Subjecting the prepared nanomaterials and nanocomposites to the XRD, FT-IR, Raman, SEM, EDX and XPS spectroscopies to understand its structural compositions and its morphology.
- Investigating the electrochemical performances such as cyclic voltammetry, galvanostatic charge-discharge analysis, electrochemical impedance analysis and cyclic stability to the synthesized nanomaterials and nanocomposites electrodes in Nickel foil through three electrode systems using 1M KOH electrolyte.
- Fabrication of asymmetrical supercapacitors of N-rGO//N-rGO/$ZnCo_2O_4$, N-rGO//N-rGO/$NiCo_2O_4$ and N-rGO//N-rGO/$MgCo_2O_4$ devices using synthesized hybrid electrode materials.

4. Research Problem

The primary objective of this thesis is to examine the physical and electrochemical performance of materials for electrodes based on carbon and with MCo_2O_4, (M= Zn, Ni, Mg) cobaltite's as the promising electrode materials of the future. By modifying nanocomposite structures and fabrication techniques, electrode materials demonstrated that they are continuously improving. The Hummer's oxidation process have been used to synthesis graphene oxide from graphite powder. By using pressurized thermal treatment in autoclaves, we followed the straightforward reduction of graphene oxides without the use of any chemical agent. Doping and simultaneous graphene oxide reduction have been planned and carried out in a manner similar to that of reduced graphene oxide synthesis. The doping agent was pentavalent nitrogen rich precursor urea. Therefore, in order to develop and uncover novel

functions for graphene oxide (GO) and widen the range of potential applications, nitrogen (N) heteroatom can be doped and reduced hydrothermally at 180ºC and also thermally at 350ºC. The major aims of this research were to explore the structural, spectral, and electrochemical changes of graphene oxide caused by doping and the application of heat as well as with its metal cobaltite nanocomposites for electrochemical energy storage applications. The two-dimensional GO, rGO, N-rGO, sheets that have been made and annealed to 350°C and investigated. It has been expected that graphene oxide (GO) becomes reduced graphene oxide under the thermal treatment of 350ºC and simultaneously N-rGO nanocomposites can effectively enhance the electrochemical activities with metal ions to promote uniform dispersion for conduction, resulting in significantly increased ionic conductivity. The higher cost always a difficulty to commercialize the technology and overcome this issue, the low temperature reflux method has been used to synthesize, ternary cobaltite MCo_2O_4 (M=Zn, Ni and Mg) and its nanocomposites. Further, the low amount of graphene oxide with N dopant of graphene oxides have been used to construct the nanocomposites of GO/MCo_2O_4, (M= Zn, Ni, Mg) and N-rGO/MCo_2O_4, (M= Zn, Ni, Mg).

GO/MCo_2O_4 nanocomposite has been prepared using a simple chemical reflux method. The prepared GO powders are sonicated 2 hrs separately. $Co(NO_3)_2.6H_2O$ and $M(NO_3)_2.6H_2O$ salts are dissolved (M=Zn, Ni, Mg) and well stirred in deionized water separately. Those two metal nitrate solutions are mixed one by one into the GO solution and made homogeneous. Then, NaOH solution is added to it. The solution is to be stirred for 1 hrs to take place the reactions completely and allowed to form the metal cobaltite, which also disperses of it on the two-dimensional graphene oxide. Further, the solution is transferred into the round bottom flask and refluxed for 3 hrs at 120ºC to have better hybridization of the aforesaid. It yields an intermediate of GO/MCo_2O_4 and it is washed and can be dried at 60 ºC. The intermediate hydroxide phase of MCo_2O_4 will be improved to the expected phase of crystallinity by calcination at 350ºC about 4 hrs and GO/MCo_2O_4 nanocomposites harvested. This scheme of synthesis is illustrated in Figure 1 and the reaction process is described in equations (1), (2) and (3).

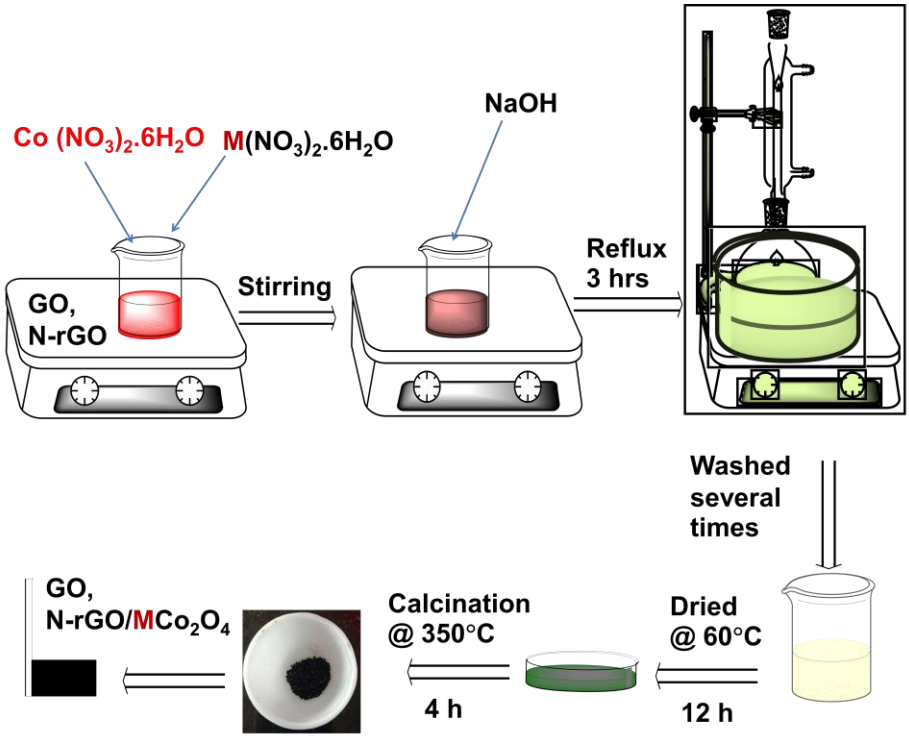

Figure 1 Synthesis scheme of GO/MCo_2O_4 and $N\text{-}rGO/MCo_2O_4$ nanocomposites

$$Co(NO_3)_2 + 2NaOH \rightarrow 2Na(NO_3) + Co(OH)_2 \quad (1)$$

$$M(NO_3)_2 + 2NaOH \rightarrow 2Na(NO_3) + M(OH)_2 \quad (2)$$

$$2M(OH)_2 + 4Co(OH)_2 + O_2 \rightarrow 2MCo_2O_4 + 6H_2O \quad (3)$$

Where, M = Zn, Ni and Mg. The same method can be followed for obtaining the $N\text{-}rGO/MCo_2O_4$ nanocomposites. The prepared GO/MCo_2O_4 and $N\text{-}rGO/MCo_2O_4$ nanocomposites are subjected to different characterizations for understanding physical, chemical and electrochemical behaviors. An electrochemical energy storage system's positive characteristics include a good specific capacitance, high power densities, and low self-discharge are observed in this research and in hybrid electrode materials fabricated and they are used to fabricate the asymmetrical supercapacitors.

5. Organization of Thesis

The above-mentioned research problem has been carried out and characterized by using various analytical methods. The work that has been done in this research is outlined in Figure 2.

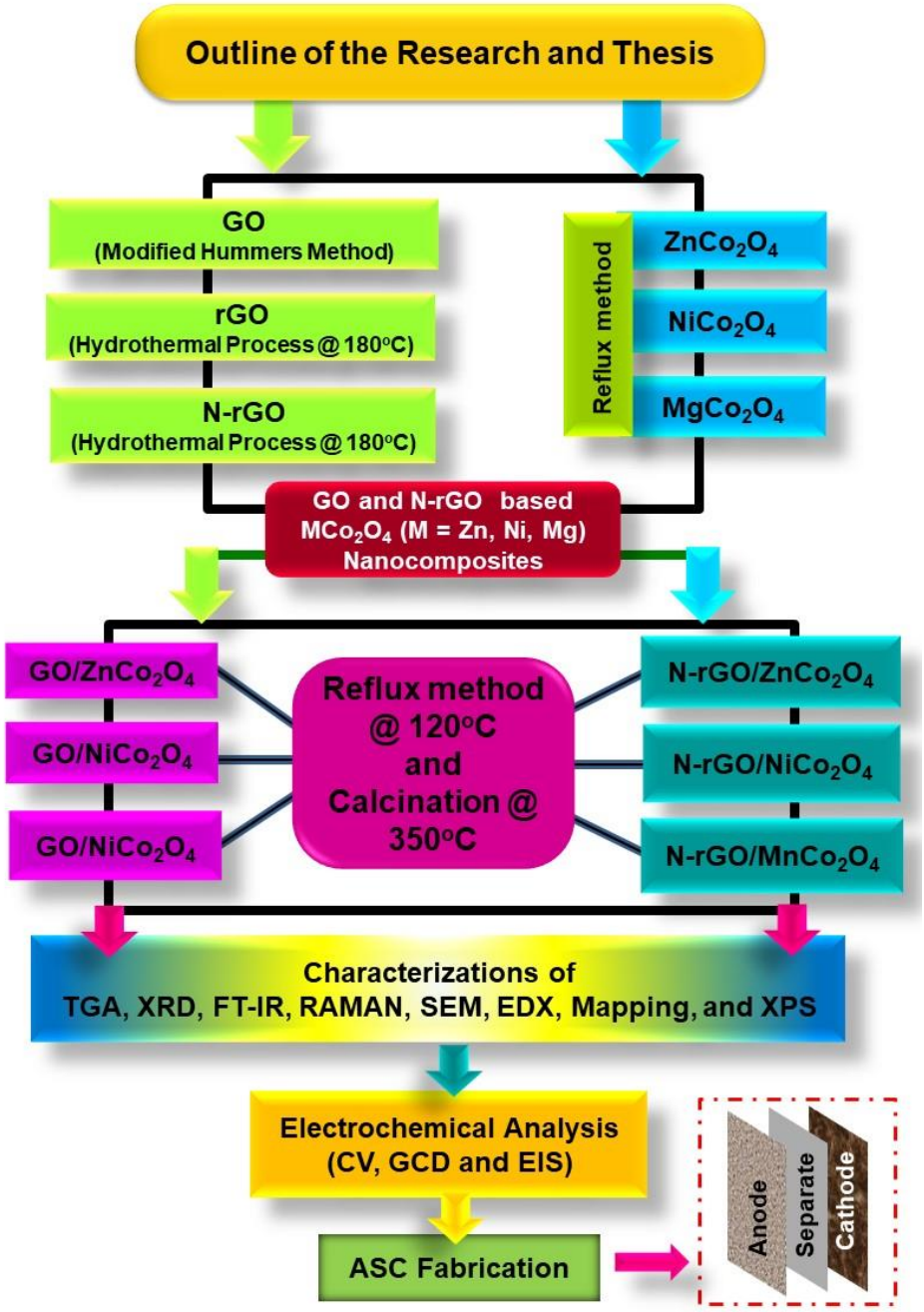

Figure 2 Schematic illustration of the outline of the research and thesis

The contents planned in the thesis are as follows,

Chapter 1 describes the requirements of energy storage systems, as well as revolutionary resources and their various types, such as batteries, supercapacitors, and fuel cells. This chapter discusses supercapacitor classifications such as electrical double layer capacitors (EDLC), pseudocapacitors (PC), and hybrid supercapacitors (HC). It is also highlighted the significance of hybrid supercapacitors. The role of nitrogen in the graphene structure and heteroatoms doped graphene oxides (GO) have

been discussed. The spinel MCo_2O_4 (M = Zn, Ni, and Mg) and its significance in electrochemical energy storage applications are discussed. In addition, a general introduction of nanoparticles is provided, as is the importance of metal oxide in energy storage applications.

Chapter 2 reviews the literature on graphene oxide, reduced graphene oxide, graphene oxide surface modification via doping and its nanocomposites with cobaltite's. The structured MCo_2O_4 (M = Zn, Ni, and Mg) metal oxides and their GO, N-rGO based nanocomposites of cobalt-based spinel have been reviewed in order to identify the research gap and area of interest for further investigation. In the review of the studied ternary metal cobaltite's, the subject of the study has been identified and discussed. The research expectations and goal of this thesis, that is hybrid electrode materials with graphene oxides have been provided. The research described here attempts to improve specific capacitance while simultaneously enhancing energy density and power density of the envisioned nanocomposites.

Chapter 3 describes the chemicals employed in the synthesis of graphene oxides and the envisioned metal cobaltite. Preparation methods such as modified Hummer's method, chemical reflux method, and hydrothermal process have also been discussed. This chapter discusses the synthesis of all the envisioned nanomaterials of graphene oxide, nitrogen doped graphene oxide, and MCo_2O_4 (M = Zn, Ni, and Mg). The synthesis of GO/MCo_2O_4 and N-rGO/MCo_2O_4 (M = Zn, Ni, and Mg) nanocomposites has also been shown. TG-DTA, XRD, FT-IR, Raman, SEM, EDX, mapping, XPS and electrochemical studies have been conducted on the developed nanomaterials and nanocomposites for understanding the physical, chemical, structural properties. This chapter also discusses the process behind the aforementioned characterization.

Chapter 4 presents the effects of nitrogen doping and annealing on graphene oxide for energy storage applications. X-ray diffraction, FT-IR, and Raman spectroscopy have been utilized to investigate the made graphene oxide, nitrogen doped graphene oxides, and surface modifications. The reduction of graphene oxides has been confirmed by variations in location and intensity changes of the D and G bands. The carbon-oxygen ratio, as well as nitrogen doping into two-dimensional graphene oxide, has been identified using EDX and mapping analysis.

A three-electrode setup in 1 M KOH electrolyte has been utilized to explore the electrochemical characteristics of undoped and doped graphene oxides. It demonstrates how doping and reduction increase graphene oxide current conduction. After being synthesized and reduced at 350°C, the specific capacitance of N-rGO has been found to be 850 Fg^{-1} and 891 Fg^{-1} respectively. It has been estimated and explained how doped and undoped graphene oxides will perform in charge-discharge analysis, cycle stability, and impedances for the relevant frequency ranges.

Chapter 5 describes the study on GO/$ZnCo_2O_4$ and N-rGO/$ZnCo_2O_4$ nanocomposites for high performance supercapacitor application prepared via chemical reflux method. The synthesized GO/$ZnCo_2O_4$ and N-rGO/$ZnCo_2O_4$ nanocomposite's crystal structure and phase purity have been studied using X-ray diffraction. $ZnCo_2O_4$ nanoparticles and nanocomposites surface morphology has been studied. It has been used to look at elemental compositions using the EDX spectrum. The N-rGO/$ZnCo_2O_4$ nanocomposite has specific capacitances from cyclic voltammetry and galvanostatic charge discharge of 1086 Fg^{-1} and 950 Fg^{-1}, respectively. Retention stability of about 89.6% is discovered after 5000 cycles. N-rGO/$ZnCo_2O_4$ is thought to have energy and power densities of 21 $Whkg^{-1}$ and 1500 Wkg^{-1} respectively. In this chapter, an asymmetric supercapacitor comprised of N-rGO//N-rGO/$ZnCo_2O_4$ has been constructed, examined and detailed.

Chapter 6 discusses the study on GO/$NiCo_2O_4$ and N-rGO/$NiCo_2O_4$ nanocomposites for hybrid supercapacitor application. Investigations using powder X-ray diffraction confirmed the structure of the synthesized nanomaterials. Using infrared and Raman spectroscopy, the bonding vibrations of the synthesized nanocomposites are verified. The composition and constituent weights of the nanocomposites have been identified using EDX analysis. Using an electrolyte of 1M KOH, the electrochemical characteristics of the nanomaterials have been assessed. Cyclic voltammetry test for N-rGO/$NiCo_2O_4$ showed a specific capacitance of 1078.2 Fg^{-1} at 5mVs^{-1} scan rate. The N-rGO/$NiCo_2O_4$ nanocomposite energy and power density have been determined to be 20.4 $Whkg^{-1}$ and 1300 Wkg^{-1} respectively. The results are reported in this chapter for the N-rGO//N-rGO/$NiCo_2O_4$ asymmetric supercapacitor (ASC) device, which has an energy density of 14.9 $Whkg^{-1}$ and a power density of 3500 Wkg^{-1}.

Chapter 7 discusses the study on GO/$MgCo_2O_4$ and N-rGO/$MgCo_2O_4$ nanocomposites for enhanced hybrid supercapacitor electrodes. The synthesized nanomaterials phase purity has been studied using XRD, FT-IR, and Raman spectra. The morphology and components of the synthesized nanomaterials are known using SEM and EDX analysis. All of the nanocomposites electrochemical capabilities have been studied in a 1M KOH electrolyte. Discussions have been made on the results of cyclic voltammetry, charge-discharge, impedance spectra, cyclic stability of $MgCo_2O_4$, GO/$MgCo_2O_4$ and N-rGO/$MgCo_2O_4$. There has been a comparison of energy and power density. N-rGO//N-rGO/$MgCo_2O_4$ asymmetric supercapacitor (ASC) has been constructed and studied. The data has been reported in this chapter and it shows an energy, power density of 28.3 $WhKg^{-1}$, 3750 WKg^{-1}.

Chapter 8 presents the summary and conclusions of the research carried out and presented in this thesis. The executive summary explains how heat reduction of graphene oxides enhances the performance of electrodes and its effects in the nanocomposites prepared. N-rGO/$ZnCo_2O_4$, N-rGO/$NiCo_2O_4$, and N-rGO/$MgCo_2O_4$ are demonstrated exceptional electrochemical performances when compared to other nanomaterials synthesized and they are summarized. This chapter also includes a summary of the findings from the fabrication of asymmetric supercapacitors. The possibility of the applications out from the results are presented as a conclusion in this chapter. The scope for future work on this area of interest is also provided.

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List of Publications

1. **G. Vignesh,** P. Devendran, N. Nallamuthu, S. Sudhahar, P.S. Kumar, and M.K. Kumar, Effects of Nitrogen, Sulphur, and Temperature Treatments on the Spectral, Structural, and Electrochemical Characteristics of Graphene Oxide for Energy Storage Applications, *Carbon Trends*, **11** (2023), 100262.

2. **G. Vignesh,** R. Ranjithkumar, P. Devendran, N. Nallamuthu, S. Sudhahar, and M. Krishna Kumar, Nitrogen Doped Reduced Graphene Oxide/$ZnCo_2O_4$ Nanocomposite Electrode for Hybrid Supercapacitor Application, *Materials Science and Engineering: B*, **290** (12) (2023), 116328.

3. **G. Vignesh,** P. Devendran, N. Nallamuthu, S. Sudhahar, and M.K. Kumar, N-rGO/$NiCo_2O_4$ Nanocomposite for High Performance Supercapacitor Applications, *Journal of Materials Science: Materials in Electronics*, **34** (9) (2023), 820.

4. **G. Vignesh,** R. Ranjithkumar, P. Devendran, N. Nallamuthu, S. Sudhahar and M. K. Kumar, Structural, Spectral, and Electrochemical Investigations of a Nitrogen-Doped N-rGO/$MgCo_2O_4$ Nanocomposite for Supercapacitor Applications. *Chemistry Select*, **8** (7), e202203915.